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The spatiotemporal variation and control mechanism of surface $p\text{CO}_2$ in winter in Jiaozhou Bay, China

Yunxiao Li^a, Hong Yang^b, Longjun Zhang^{c*}, Xufeng Yang^d, Han Zang^e, Wenhua Fan^a, Gailing Wang^a

^a Environment Science Laboratory, College of Resource and Environment, Shanxi Agricultural University, Taigu 030801, China

^b Department of Geography and Environmental Science, University of Reading, Whiteknights,
Reading RG6 6AB, UK

^cKey Laboratory of Marine Environmental Science and Ecology, Ministry of Education, College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

^d Second Institute of Oceanography, Ministry of Natural Resources, Hangzhou 310012, China

^e College of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

*Corresponding author at: College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China.

E-mail address: longjunz@ouc.edu.cn (L Zhang).

Abstract

In many mid-latitude coastal waters during winter months, in addition to temperature, the large change in biogeochemical processes often influence and complicate the surface partial pressure of CO_2 ($p\text{CO}_2$). Based on the hydrological and carbonate parameters in seven cruises, this study analysed the evolution process and explored the control mechanism of the surface $p\text{CO}_2$ in Jiaozhou Bay, China, from December to March. The results showed that the $p\text{CO}_2$ ranged from 157 μatm to 647 μatm , and the bay represented a sink for atmospheric CO_2 ($-3.8 \text{ mmol m}^{-2} \text{ d}^{-1}$) in the whole winter. The non-temperature processes were the dominant factors affecting intra-winter $p\text{CO}_2$ variation. In December, the bay was dominated by aerobic respiration and acted as a CO_2 source ($3.0 \text{ mmol m}^{-2} \text{ d}^{-1}$). From early January to late February, however, the vigorous growth of cold algae caused strong primary production, and the bay presented as a CO_2 sink (from $-6.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ in early January to $-15.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ in late February). In March, primary production weakened and the effects of the CaCO_3 precipitation appeared, and the strength of the CO_2 sink was obviously weakened ($-1.1 \text{ mmol m}^{-2} \text{ d}^{-1}$). Meanwhile, the water temperature decreased gradually from December to late January and then increased until March, and it further expanded the variation range of $p\text{CO}_2$. Our results highlight the obvious source/sink change in mid-latitude seawater CO_2 in winter, while more field observations are still needed to further understand the complicated biogeochemical processes and its influence on seawater $p\text{CO}_2$.

Keywords: $p\text{CO}_2$; Aerobic respiration; Primary production; CaCO_3 precipitation; Controlling mechanism; Jiaozhou Bay

1. Introduction

The absorption intensity of CO_2 in coastal waters has received increasing attention (Borges, 2011; Cai et al., 2011; Gruber, 2015). The current estimate accounts for 10~20% of the CO_2 absorbed by the world's oceans (Chen et al., 2013; Laruelle et al., 2014; Wanninkhof et al., 2013). However, the rapid change in biogeochemical processes produces large uncertainties in the estimates. Therefore, a more comprehensive and in-depth understanding of the spatiotemporal pattern and mechanisms controlling coastal CO_2 system is extremely necessary.

In winter, a decrease in seawater temperature increases the solubility of CO₂, resulting in a decrease in the surface partial pressure of CO₂ ($p\text{CO}_2$). In most of the mid-latitude sea areas in the world, the temperature variation from summer to winter accounts for more than 50% of the change in $p\text{CO}_2$ (Takahashi et al., 2002). Many studied areas, such as the western area of the North Atlantic Ocean (Heike et al., 2004), the North Sea (Thomas et al., 2005), the US South Atlantic Bight (Jiang et al., 2013) and the North Yellow Sea (Xue et al., 2012), have shown that low temperature in winter often results in low $p\text{CO}_2$ levels, and some ocean areas even appear as sinks of atmospheric CO₂. However, affected by the coupled influence of low temperature, vertical mixing, runoff variation, nutrient supply and light intensity in winter, vigorous growth of phytoplankton often occurs in many mid-latitude coastal waters, such as the waters near Blanca (Argentina) in South America (Popovich et al., 2008), the Narragansett Bay and the Sargasso Sea in North America (Oviatt et al., 2002; Tin et al., 2016), the waters near the Loire estuary and the Adriatic Sea in Europe (Guillaud et al., 2008; Ljubimir et al., 2017), and the nearshore areas of the Bohai Sea and the Hokkaido in North-east Asia (Sakamoto et al., 2008; Zhao et al., 2004). In addition, a certain degree of aerobic respiration occurs in some areas, for example, the central area of the Baltic Sea and the North Yellow Sea (Wesslander et al., 2010; Xu et al., 2016). Therefore, in addition to the effects of temperature variation, the influence of non-temperature biogeochemical processes on the CO₂ source/sink change should not be neglected in mid-latitude coastal waters in winter.

The CO₂ sinks caused by primary production in winter have been reported in some mid-latitude coastal waters. In the Patagonia Sea in South America, Bianchi et al. (2009) conducted a cruise survey in winter. Their results showed that $p\text{CO}_2$ values had a significant negative correlation with Chlorophyll *a* (Chl *a*), and the region of 60~61.1°W with the highest Chl *a* value of >3.5 µg/L acted as a sink of atmospheric CO₂. In the nearshore areas of the Loire estuary, based on one cruise data in February, Bozec et al. (2012) found that the increase in river discharge promoted the vertical stratification of seawater and brought large amounts of nutrients. Consequently, the phytoplankton bloom consisting mainly of diatoms caused the seawater surface $p\text{CO}_2$ to be lower than the atmosphere by 42 µatm. Regarding the phenomenon of an increase in $p\text{CO}_2$ caused by aerobic respiration, Xu et al. (2016) found that vertical mixing carried the subsurface organic matter to the

surface layer and aerobic respiration made the northern Yellow Sea act as a CO₂ source in December (the average $p\text{CO}_2$ was 464 μatm). In spite of some field observation in different areas, more cruise surveys and analyses are still needed to more comprehensively reveal the detailed spatiotemporal pattern of $p\text{CO}_2$ and its control mechanisms throughout the winter months.

Jiaozhou Bay (JZB) (35°18'~36°18'N, 120°04'~120°23'E) is a typical mid-latitude semi-closed shallow water in northern China. The water area is 302.9 km² and the average water depth is 7 m. The climate is dominated by the East Asia Monsoon, with northerly wind in winter and southerly wind in summer (Li et al., 2006). The tidal current is a regular semi-diurnal tide that induces strong vertical mixing and good vertical homogeneity of the seawater temperature and salinity (Chen et al., 1999; Liu et al., 2004). The bay is an ideal area for characterizing the natural variation in $p\text{CO}_2$ and understanding their controlling processes, particularly in winter. First, as a typical mid-latitude water body, JZB has a strong seasonal change of physically properties. In particular, the average seawater surface temperature increases by ~ 10 °C from winter to spring (Li et al., 2007). Second, approximately 37% of the human population in the world lives within 100 km of the coastline (Cohen et al., 1997) and especially in the mid-latitude area, making this area subject to intense human impact (Bauer et al., 2013). JZB is a typical bay that is highly affected by urbanization. The eastern area of the bay is adjacent to the downtown of Qingdao City, with a population of 4.8 million, and the major estuaries (Licun River, Haibo River and Loushan River) have already become conduits for wastewater (Gao et al., 2008). Large amounts of nutrient and organic pollutant input have caused eutrophication and other problems in the JZB, with strong influence on carbon cycle in the area (Wang and Wang, 2011). The measurement of phytoplankton biomass, determined by using Chl *a*, in the past two decades indicated a clear bimodal pattern with peaks in summer and winter in the bay (Sun et al., 2011a; Wang et al., 2015; Wu et al., 2004). Same as many coasts in China, JZB is also an important shellfish-farming area with a breeding area of 107 km² (Yang et al., 2007; Zhang et al., 2005), suggesting the possible effect of calcification on $p\text{CO}_2$.

In the previous studies on controlling mechanisms of $p\text{CO}_2$ in the JZB during winter, Zhang et al. (2012) conducted one cruise in autumn and the other in winter. Their results indicated that the

bay experienced a process of intense organic degradation in autumn and strong primary production in winter, causing the bay from a CO₂ source to a sink during the period. Recently, Zang et al. (2018) found that the decrease in seawater temperature and enhancement of primary production together resulted in the bay acting as a CO₂ sink. However, *p*CO₂ changes throughout the winter and the mechanism for the variation are far from clearly understood. To fill the knowledge gap, this study researched the variation in seawater surface *p*CO₂ from December to March in the JZB and explored the factors determining the change of *p*CO₂. In particular, this study analysed the effect of the biogeochemical process induced by phytoplankton bloom on CO₂ source/sink patterns, with the consideration of water temperature variation (decrease first and increase later). The results can improve the understanding of the *p*CO₂ control mechanism in mid-latitude coastal waters where strong biological activities occur in winter.

2. Material and methods

2.1 Survey stations and sample processing

Seven cruises were conducted in the JZB during winter from 2008 to 2016. Survey time and number of stations are listed in Table 1. In each cruise, samples were collected from 24~33 stations (Figure 1). During the cruises, seawater samples were collected from the water surface at a depth of approximately 1.5 m because of the homogeneous vertical profiles in the JZB water column (Chen et al., 1999). Seawater surface temperature, salinity, oxygen saturation (DO%) and *p*CO₂ data were collected continuously, and discrete water samples were collected using 5 L Niskin bottles for later analysis of dissolved inorganic carbon (DIC), total alkalinity (TA), and Chl *a*.

Surface temperature and salinity were measured using a SBE 45 Micro TSG (Sea-Bird, Inc., Bellevue, WA, USA), with a nominal precision of 0.002 °C for temperature and 0.005 for salinity. The DO% was measured with a YSI-5000 oxygen analyser (YSI Corporation, Yellow Spring, OH, USA), which was calibrated using the Winkler titration method (nominal precision: 0.1%). The surface *p*CO₂ was measured with a non-dispersive infrared (NDIR) spectrometer (Li-Cor Model Li-7000, Lincoln, NE, USA) or a G2131-I Analyser (PICAROO, USA) using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS), coupled to an equilibrator. The *p*CO₂ data in cruises before 2014 were measured using a Li-7000 NDIR spectrometer with a measurement uncertainty of

less than 1%, and those in 2014 and after were measured using a G2131-I Analyser with a nominal precision of < 50 ppbv over 5-min intervals. Before and after each cruise, the $p\text{CO}_2$ measurement instruments were calibrated against three CO_2 gas standards (202, 401 and 1010 ppm CO_2 in air) and one N_2 reference (National Research Center for Certified Reference Materials, Beijing, China).

To measure DIC and TA of water samples, filtration treatment was needed to avoid the influence of the particular matter. The DIC samples were directly collected from the Niskin bottles using a syringe and filtered through a 0.45 μm disposable syringe filter to avoid exchange with the air. TA samples were filtered through cellulose acetate membranes (0.45 μm) using a borosilicate glass filter. The DIC and TA samples were all poisoned with saturated mercury chloride (final concentration: c. 0.02% by volume) and preserved at 4 °C (Li et al., 2017). The DIC values were determined by acid extraction using a total organic analyser (TOC-VCPN, Shimadzu Corporation, Kyoto, Japan) (Liu et al., 2014) or a DIC analyser (AS-C2, Apollo SciTech, USA). The TA values were determined by Gran titration using a Total Alkalinity Titrator (AS-ALK2, Apollo SciTech, USA). Measurements of DIC and TA were both calibrated against Certified Reference Materials (CRMs) from Scripps Institution of Oceanography at a precision and accuracy level of 0.2%.

Samples for Chl *a* measurement were filtered through GF/F glass fibre membranes (0.7 μm ; Whatman, Maidstone, UK) at pressures below 0.04 MPa. Saturated magnesium carbonate was added to the membranes after filtration, and the samples were preserved at -20 °C. Before analysis, the samples were extracted with 90% acetone, and the supernatant fluid was analysed using a fluorescence spectrophotometer (F4500, Hitachi Co, Tokyo, Japan).

2.2. Methodology

2.2.1. Aragonite saturation state

The aragonite saturation state (Ω_{arag}) at *in situ* temperatures ($\Omega_{\text{arag}}@_{\text{situ}}$) was calculated from the DIC, TA, *in situ* temperature, and *in situ* salinity values using the CO_2 program (Lewis and Wallace, 1998) and the CO_2 system coefficients of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987). The K_{sp}^* values for aragonite were taken from Mucci (1983), and the Ca^{2+} concentrations were assumed to be proportional to salinity, as presented in Millero (1979).

2.2.2. $p\text{CO}_2$ normalization

Considering that our $p\text{CO}_2$ data were collected over several years, this study normalized the surface water $p\text{CO}_2$ values of the cruises in December to the year 2015 and those of other cruises to the year 2016 by assuming that seawater surface $p\text{CO}_2$ increased at the same growth rate ($1.5 \mu\text{atm yr}^{-1}$) of the $p\text{CO}_2$ in the air according to Nakaoka et al. (2006).

2.2.3. The temperature effect on $p\text{CO}_2$

To assess the temperature effect on the distribution of $p\text{CO}_2$ in each cruise, this study normalized the observed *in situ* $p\text{CO}_2$ data to the average seawater temperature of the corresponding cruise using the equations proposed by Takahashi et al. (1993), and then temperature-normalized $p\text{CO}_2$ ($np\text{CO}_2$) was calculated:

$$np\text{CO}_2 = (p\text{CO}_2)_{\text{obs}} \times \text{EXP}[0.0423 \times (T_{\text{nor}} - T_{\text{obs}})] \quad (1)$$

where $(p\text{CO}_2)_{\text{obs}}$, T_{obs} and T_{nor} are the observed *in situ* surface $p\text{CO}_2$, *in situ* temperature and the temperature to which the *in situ* $p\text{CO}_2$ needs to be normalized, respectively. Then, the difference between $np\text{CO}_2$ and $(p\text{CO}_2)_{\text{obs}}$ was the temperature effect on $p\text{CO}_2$ distribution in the cruise.

Similarly, to assess the temperature effect on $p\text{CO}_2$ between the cruises, the average $p\text{CO}_2$ for each cruise was normalized to the average seawater temperature of all cruises. Then, the $p\text{CO}_2$ in each cruise under the average seawater temperature in winter ($Np\text{CO}_2$) was calculated:

$$Np\text{CO}_2 = (p\text{CO}_2)_{\text{mean}} \times \text{EXP}[0.0423 \times (T_{\text{Mean}} - T_{\text{mean}})] \quad (2)$$

where $(p\text{CO}_2)_{\text{mean}}$ and T_{mean} are the average surface $p\text{CO}_2$ and temperature in each cruise. T_{Mean} is the average seawater temperature of all cruises.

To assess the relative importance of temperature and non-temperature effect (including the effect of biological activities) on $p\text{CO}_2$ between the cruises, this study used equations developed by Takahashi et al. (2002):

$$\text{T: } p\text{CO}_2 \text{ at } T_{\text{obs}} = (p\text{CO}_2)_{\text{Mean}} \times \text{EXP}[0.0423 \times (T_{\text{obs}} - T_{\text{Mean}})] \quad (3)$$

$$\text{B: } p\text{CO}_2 \text{ at } T_{\text{Mean}} = (p\text{CO}_2)_{\text{obs}} \times \text{EXP}[0.0423 \times (T_{\text{Mean}} - T_{\text{obs}})] \quad (4)$$

$$\Delta(p\text{CO}_2)_{\text{non-temp}} = (p\text{CO}_2 \text{ at } T_{\text{Mean}})_{\text{max}} - (p\text{CO}_2 \text{ at } T_{\text{Mean}})_{\text{min}} \quad (5)$$

$$\Delta(p\text{CO}_2)_{\text{temp}} = (p\text{CO}_2 \text{ at } T_{\text{obs}})_{\text{max}} - (p\text{CO}_2 \text{ at } T_{\text{obs}})_{\text{min}} \quad (6)$$

where $(pCO_2)_{Mean}$ is the average pCO_2 of all cruises, and the subscripts “max” and “min” indicated the maximum and minimum values, respectively.

The relative importance of each effect can be expressed in terms of the ratio between the temperature effect (T) and non-temperature effect (B):

$$T / B = \Delta(pCO_2)_{temp} / \Delta(pCO_2)_{non-temp} \quad (7)$$

2.2.4. Statistical analyses

The correlations between environmental variables were analysed using SPSS 21 (IBM SPSS Statistics, IBM Corporation, Armonk, New York). All statistical analyses were at significance level of 0.05.

3. Results

3.1 Temperature and salinity

The seawater temperature in the JZB in winter is shown in Figure 2. The temperatures in the seven cruises surveyed were all below 10 °C, and the average temperature decreased from 7.1 °C in December to 1.5 °C in late January and then gradually increased to 8.6 °C in March. The time span of seven cruises (8 years) was relatively large. Compared with the multi-year diurnal average seawater temperature data in the JZB during winter, the temperature in the five cruises from December to late January was slightly lower and that in March. Even so, the overall variation trends of temperature in these cruises were consistent with the changes of daily seawater temperature, showing that these cruise data had a certain representativeness and can be used to analyse the pCO_2 variation between winter months in the JZB. The temperature increased from the upper end of the bay to the mouth of the bay in the five cruises from December to late January (Figure 3). The temperature gradient in each cruise in this period was relatively large, and the difference between the lowest and the highest temperature values all exceeded 4.0 °C. The temperature values in the two cruises during December were the highest (4.4~9.0 °C and 3.9~9.7 °C), while the temperature values in the cruise in late January were the lowest (-1.3~4.6 °C). In late February, due to the impact of land warming, no obvious temperature difference between the upper end of the bay and the mouth area existed. The temperature in this period was evenly distributed with a range of 3.8~4.7 °C. In

March, the temperature decreased from the upper end of the bay to the mouth, with a range of 7.7~9.9 °C.

The seawater surface salinity values in December and early January were relatively close and were basically between 29.0 and 30.9 (Figure 2). In the four cruises from mid-January to March, the salinity levels were higher with values of >30.3. In late January, the salinity values were the highest throughout the winter and ranged from 30.9 to 31.7. In late February and March, the salinity decreased slightly, and the ranges were 30.3~31.2 and 30.5~31.2, respectively. In terms of distribution in these seven cruises (Figure 3), the salinity increased from the northeastern area to the mouth, and the difference between the highest and lowest values in each cruise was less than 2.0. The salinity in the northeastern area was always the lowest, and the gradient variation was relatively large, indicating the influence of terrestrial input. The rivers entering the JZB have no natural runoff and the winter is the dry season. However, three wastewater treatment plants located near the northeastern area and the daily total amount of treated sewage is up to ~510000 tons, indicating that the direct treated sewage input was the main reason for the low salinity in this region.

3.2 $p\text{CO}_2$

The distribution of seawater surface $p\text{CO}_2$ in the JZB in winter is shown in Figure 4. According to the average air CO_2 data (408 μatm) from December 2015 to March 2016 from the flask measurements on the Tae-ahn Peninsula (126.131°E, 36.731°N) adjacent to the southern Yellow Sea, the bay in two cruises during December acted as a source of atmospheric CO_2 as a whole, and the $p\text{CO}_2$ ranges were 379~536 μatm and 382~647 μatm , respectively. The $p\text{CO}_2$ gradually decreased from the northeastern area to the mouth area. Obviously, the $p\text{CO}_2$ in the northeastern area was the largest (>450 μatm). In early January, the $p\text{CO}_2$ value was between 216 μatm and 520 μatm . The northeastern area also acted as a CO_2 source, but the western area was unsaturated with respect to atmospheric CO_2 . In mid-January (282~375 μatm), late January (202~324 μatm) and late February (157~327 μatm), the CO_2 levels in the entire bay were all unsaturated and the $p\text{CO}_2$ decreased from the mouth to the northeastern area. The $p\text{CO}_2$ value in the northeastern area was even below 190 μatm in late February. In March, the bay acted as a weak CO_2 sink as a whole with the $p\text{CO}_2$ values of 357~415 μatm . The $p\text{CO}_2$ value was highest in the northern area and decreased gradually to the

mouth area, while the difference of $p\text{CO}_2$ between areas did not exceed 50 μatm . Overall, the $p\text{CO}_2$ values throughout the winter showed a process of gradual decrease from December to the end of February and then obvious increase in March (Figure 4h). The average $p\text{CO}_2$ value of all cruises was 352 μatm . Therefore, the bay acted as a sink of atmospheric CO_2 in winter as a whole.

3.3 DO% and Chl *a*

The distribution of seawater surface DO% in the JZB in winter is shown in Figure 5. The seawater surface DO in the JZB was unsaturated in both cruises in December (ranges: 79.8~98.1% and 79.5~101.5%) and increased from the northeastern area to the mouth area. In the northeastern area, which acted as the strongest CO_2 source, the unsaturated degree of DO was the highest and the DO% values were approximately 85%, showing the presence of aerobic respiration. In early January, DO remained unsaturated in the northeastern area which acted as a CO_2 source, but oversaturated (~105%) in the western area which acted as a CO_2 sink. In mid-January, late January and late February, when the entire JZB acted as a CO_2 sink, the DO% ranges were 101.0~117.5%, 109.4~120.2% and 102.0~147.0%, respectively. In these three cruises, DO was oversaturated and decreased from the northeastern area to the mouth area. Moreover, in the northeastern area, DO% values were highest and were above 110% (mid-January), 115% (late January) and 125% (late February), respectively, showing a strong primary production process. In March, the DO was slightly oversaturated with DO% values of 103.2~114.8%. The DO% distribution in the bay was relatively uniform, and the values in most areas were approximately 109.0%. Overall, the variation trend of DO% throughout the winter was opposite to $p\text{CO}_2$, a process of gradual increase from December to late February and then decrease in March (Figure 5h).

The distribution of seawater surface Chl *a* in the JZB in winter is shown in Figure 5. The Chl *a* concentration was low and below 0.60 $\mu\text{g/L}$ in December when the DO was unsaturated. The ranges of Chl *a* in these two cruises were 0.03~0.61 $\mu\text{g/L}$ and 0.12~0.55 $\mu\text{g/L}$, respectively. In early January, the Chl *a* concentrations in the western and mouth areas were above 0.60 $\mu\text{g/L}$. In mid-January, late January and late February, when the DO in the entire bay was oversaturated, the ranges of Chl *a* were 0.30~2.30 $\mu\text{g/L}$, 0.40~9.12 $\mu\text{g/L}$ and 1.78~8.94 $\mu\text{g/L}$, respectively. The Chl *a* concentrations in the three cruises all decreased from the northeastern area to the mouth, and the

Chl *a* concentrations in the northeastern area were above 1.50 µg/L, 4.50 µg/L and 6.50 µg/L, respectively. In March, when the DO was slightly oversaturated, the Chl *a* concentration was lower with Chl *a* values of 0.04~0.40 µg/L. Overall, the variation of phytoplankton biomass represented by Chl *a* concentration throughout the winter was in good agreement with that of DO%, showing a process of gradual increase from December to the end of February and then obvious decrease in March (Figure 5h).

3.4 DIC and TA

The seawater surface DIC in the JZB in winter is shown in Figure 6. In December and early January, the DIC levels were relatively high and generally ranged between 2100 µmol/kg and 2300 µmol/kg. The DIC values were highest in the northeastern area and decreased gradually to the mouth, with the difference of approximately 150 µmol/kg. In these two periods, the difference in DIC distribution mainly occurred in the western area of the bay. In December, the DIC in the western area was approximately 40 µmol/kg higher than that in the mouth, but they were close in early January. In middle and late January, the DIC values (2142~2156 µmol/kg and 2130~2155 µmol/kg) were lower than those in December. The DIC also decreased from the northeastern area to the mouth area, but the difference between two areas was much smaller, just ~15 µmol/kg. In late February, the DIC values were the lowest throughout the winter, with a range of 2000~2140 µmol/kg. The DIC value increased gradually from the northeastern area to the mouth area and the difference was up to ~90 µmol/kg. In March, the DIC values (2085~2126 µmol/kg) also maintained a lower level but increased from the north area to the mouth area, with the difference of ~20 µmol/kg between two areas.

Seawater surface TA in the JZB during winter is shown in Figure 6. In December and early January, the TA values ranged generally between 2240 µmol/kg and 2400 µmol/kg. The spatial distribution of TA was similar to that of DIC. The TA values were also highest in the northeastern area and decreased gradually to the mouth. However, the decreasing gradient of TA was slightly smaller than that of DIC, and the TA difference between the northeastern and the mouth area was approximately 110 µmol/kg. In early January, TA values in the western area (where DIC values were close to those in the mouth area) were ~30 µmol/kg higher than those in the mouth area. In middle

and late January, the TA ranges were 2297~2336 $\mu\text{mol/kg}$ and 2302 ~2360 $\mu\text{mol/kg}$, respectively. Compared to December, the TA values of these two cruises were slightly higher in most areas except for the northeastern area, and the TA difference between the northeastern area and the mouth area was only ~45 $\mu\text{mol/kg}$. In late February, the TA was between 2302 $\mu\text{mol/kg}$ and 2364 $\mu\text{mol/kg}$, and the spatial distribution was opposite to that of DIC. The TA value was highest in the northeastern area with low DIC and increased gradually to the mouth area. In March, the TA value ranged from 2290 $\mu\text{mol/kg}$ to 2347 $\mu\text{mol/kg}$. Spatial distribution of TA was similar to that of DIC, and the TA values increased from the northern area to the mouth area. However, the change gradient of TA was larger than that of DIC, and the TA values in the northern area were ~40 $\mu\text{mol/kg}$ lower than those in the mouth.

4. Discussion

4.1 The temperature effect on variation in surface $p\text{CO}_2$ in the JZB during winter

Temperature is an important thermodynamic parameter affecting seawater $p\text{CO}_2$. For example, the relationship between seawater temperature and $p\text{CO}_2$ proposed by Takahashi et al. (1993) shows that $p\text{CO}_2$ decreases by approximately 4.23% for every 1 $^{\circ}\text{C}$ decrease in water temperature. To assess the temperature effect on the $p\text{CO}_2$ distribution for each cruise, this study calculated $np\text{CO}_2$ by normalizing the surface $p\text{CO}_2$ at each station to the average seawater temperature in the corresponding cruise (see Section 2.3.3 Methodology). As shown in Figure 7a-g, in December (13th and 21st), early January (8th), mid-January (21st), and late January (26th), the $p\text{CO}_2$ in the upper end of the bay with lower temperatures increased by 20~65 μatm after normalization, while the $p\text{CO}_2$ in the mouth area of the bay with higher temperatures decreased by 15~30 μatm . This indicated that surface $p\text{CO}_2$ in the nearshore area was relatively low due to the cooling effect of land, whereas that in the mouth area was higher due to the frequent water exchange with the Yellow Sea where water temperature was relatively higher. In March (25th), the $p\text{CO}_2$ in the upper end of the bay with higher temperature decreased by ~12 μatm after normalization, while the $p\text{CO}_2$ in the mouth area with lower temperature increased by ~12 μatm , suggesting that land warming resulted in higher $p\text{CO}_2$ in the upper end area. All these results indicated the temperature effect on the spatial distribution of $p\text{CO}_2$ in certain periods of winter. However, combined with the distribution of *in situ* $p\text{CO}_2$ in each

cruise (Figure 4), in mid-January and late January, the *in situ* $p\text{CO}_2$ value in the northeastern area was lower than that in the mouth area by about $\sim 80 \mu\text{atm}$, which was larger than the contribution of $p\text{CO}_2$ ($\sim 50 \mu\text{atm}$) caused by the difference in water temperature. In March, the *in situ* $p\text{CO}_2$ value in the northeastern was higher than that in the mouth area by about $50 \mu\text{atm}$, which was also larger than the contribution of $p\text{CO}_2$ ($\sim 24 \mu\text{atm}$) caused by the difference in water temperature. This indicated that the spatial distribution of $p\text{CO}_2$ was still largely affected by other factors. Even in some cruises, temperature may not be the main factor controlling $p\text{CO}_2$ distribution. For example, in December, *in situ* $p\text{CO}_2$ was the lowest in the mouth area with higher temperatures and the highest in the northeastern waters with lower temperatures. In late February, the difference between the highest and lowest seawater temperature was only 0.9°C , but the difference in *in situ* $p\text{CO}_2$ was more than $160 \mu\text{atm}$ (Figures 4, 7).

The seawater surface temperature in the JZB experienced a pattern of first decrease and then increase from December to March. To assess the temperature effect on the $p\text{CO}_2$ variation between cruises, the NpCO_2 was calculated by normalizing the average seawater $p\text{CO}_2$ in each cruise to the average seawater temperature of all cruises (5.2°C) (see Section 2.3.3 Methodology) (Figure 8). After normalization, the $p\text{CO}_2$ decreased by $33 \mu\text{atm}$ and $51 \mu\text{atm}$ in December and March, respectively, when the temperatures were relative higher; the $p\text{CO}_2$ increased by $20 \mu\text{atm}$, $21 \mu\text{atm}$, $47 \mu\text{atm}$, and $12 \mu\text{atm}$ in early January, mid-January, late January and late February, respectively, when the temperatures were relative lower. The difference of $p\text{CO}_2$ between cruises decreased by 74% from December to early January and 52% from late February to March, but it only decreased by 8% from early January to late February. Moreover, the overall the temporal pattern of $p\text{CO}_2$ kept stable. The highest and lowest $p\text{CO}_2$ values still appeared in December and late February, respectively, and the difference between months was up to $130 \mu\text{atm}$. It indicated that the temperature effect may play an important but not a dominant role in the whole intra-winter $p\text{CO}_2$ variation. Based on the method proposed by Takahashi et al. (2002) (see Section 2.3.3 Methodology), the relative contributions of temperature (T) and non-temperature effect (B) to $p\text{CO}_2$ variation throughout the winter were calculated. It is noteworthy that this method was originally designed for open oceanic systems and the non-temperature effect could be attributed almost entirely to the “net

biology effect". However, it had been widely used by other authors to assess the role of temperature versus biological factors in the control of $p\text{CO}_2$ dynamics in coastal areas (de la Paz et al., 2009; Ribas et al., 2011). The non-temperature term for coastal waters includes all the biogeochemical processes acting on CO_2 . In this study, the T/B ratio was 0.81, indicating the main role of the non-temperature effect in intra-winter $p\text{CO}_2$ variation.

4.2 The non-conservative behaviour of DIC and TA and variation in the JZB during winter

In coastal waters, the non-temperature processes influencing $p\text{CO}_2$ mainly includes terrestrial input, biological processes (production/respiration), CaCO_3 processes (precipitation/dissolution), CO_2 sea-air exchange (evasion/invasion) and others. The occurrence of these processes often changes DIC and TA. Therefore, the analysis of DIC and TA non-conservative behaviour is helpful for identifying the main non-temperature factors for $p\text{CO}_2$ (Jiang et al., 2013; Li et al., 2017; Zhai et al., 2015). In some nearshore bays with no obvious runoff input, the ocean end-member can be used as a standard value to evaluate the effects of terrestrial input and biogeochemical processes, that is, the deviation of the measured DIC or TA from the ocean end-member. Thus, according to the approach of Jiang et al. (2013), the values for the addition or removal of DIC and TA in each cruise were obtained using the station data in the mouth area, which could represent the DIC and TA levels of the Yellow Sea, as the seawater end-member values (Li et al., 2017, Yang et al., 2018). In the specific calculation in late January, considering that the DO% in the mouth area was approximately 110% and a certain primary production existed (Figure 5e), this study chose the ocean end-member in mid-January, which was only 5 days apart. The calculation method is as follows:

$$\Delta\text{DIC} = \text{DIC}_i - \frac{S_i}{S_{\text{ocean}}} \times \text{DIC}_{\text{ocean}} \quad (8)$$

$$\Delta\text{TA} = \text{TA}_i - \frac{S_i}{S_{\text{ocean}}} \times \text{TA}_{\text{ocean}} \quad (9)$$

where ΔDIC and ΔTA represent the addition and removal of DIC and TA, respectively; and S_i (S_{ocean}), DIC_i ($\text{DIC}_{\text{ocean}}$), and TA_i (TA_{ocean}) are the salinity, DIC and TA of station i (the ocean end-member), respectively. This study used the average values of DIC and TA from the two stations, which had the highest salinity and were near the Yellow Sea, as the ocean end-member. The specific values are shown in Table 2.

As shown in Figure 9, the non-conservative behaviours of DIC and TA in the JZB presented three stages. First, Δ DIC and Δ TA maintained an addition status in the two cruises in December. The maximum addition values were observed in the northeastern area with low salinity and exceeded 200 $\mu\text{mol/kg}$, showing the effect of terrestrial DIC and TA input. The altered ratio of Δ DIC and Δ TA from terrestrial input was generally close to 1:1 (Cai et al., 2008), but the Δ DIC in the JZB was obviously larger than Δ TA in this period. Moreover, the difference between Δ DIC and Δ TA was the largest in the northeastern area (more than 90 $\mu\text{mol/kg}$), indicating that in addition to terrestrial input, other factors influenced DIC. Second, in the four cruises from early January to late February, Δ TA values also presented an addition status. However, there was a phenomenon that Δ DIC was less than Δ TA. In early January, this situation only occurred in the western area. In mid-January, this situation expanded to the entire bay. In late January and late February, the DIC showed partial or complete removal in different stations. The results indicated that DIC experienced an obvious consumption in this period. Finally, in March, both DIC and TA showed a removal status, and the removal of TA was greater than that of DIC. The maximum removals of TA and DIC were close to 30 $\mu\text{mol/kg}$ and 20 $\mu\text{mol/kg}$, respectively. This suggested that the processes consuming DIC and TA existed in the meantime. Thus, the influences of non-temperature processes on $p\text{CO}_2$ were discussed in each period separately.

4.3 Aerobic respiration caused the bay to act as a CO_2 source in early winter

The biogeochemical processes that cause the non-conservative behaviour of DIC and TA could alter Δ DIC and Δ TA in fixed ratios. By comparing the ratio of Δ TA to Δ DIC at each station with the fixed ratios of the various processes that alter Δ TA and Δ DIC, the main processes causing the non-conservative behaviour of DIC and TA can be further clarified (Cai et al., 2004; Li et al., 2017; Liu et al., 2014). Throughout the winter in the low water period, the rivers flowing into the JZB had no natural runoff and the salinity in the northeastern area of the JZB was always the lowest. Therefore, the sewage discharge from the three wastewater treatment plants became the main source of terrestrial input, and the impact ratio of Δ DIC to Δ TA was approximately 1.03:1 (Li et al., 2017). For the production/respiration, the phytoplankton preferred $\text{NH}_4\text{-N}$ as a nitrogen source in the JZB (Jiao, 1993). According to the Redfield equation with $\text{NH}_4\text{-N}$ as the nitrogen source (Redfield, 1963),

the fixed ratio of Δ DIC to Δ TA altered by this process was 106:15. The fixed ratio of TA to DIC altered by the CaCO_3 process was 2:1, and CO_2 evasion/invasion did not change TA while affected DIC. Thus, the Figure 10 can be obtained.

The Δ TA/ Δ DIC values in December were all located in the first quadrant, between the ratio lines of direct treated sewage input and aerobic respiration (Figure 10 a, b). This indicated that the DIC and TA additions were mainly caused by direct treated sewage input and aerobic respiration. The total amount of daily treated sewage from the three wastewater treatment plants near the northeastern area was 510,000 tons, and the DIC and TA concentrations of discharged sewage were as high as 2554~5173 $\mu\text{mol/kg}$ and 2326~4570 $\mu\text{mol/kg}$, respectively. Obviously, the direct input of sewage was an important factor for the addition of DIC and TA in the northeastern area (Liu et al., 2019; Yang et al., 2018). The impact of sewage on aquatic environment has been widely reported in China (Yang et al., 2008; Yang et al., 2012). Meanwhile, the DO in the entire bay was unsaturated, and the DO% was the lowest in the northeastern area with the highest $p\text{CO}_2$, which confirmed the existence of an aerobic respiration process. Moreover, since aerobic respiration had little effect on TA while increased DIC according the Redfield ratio, Δ DIC values were obviously larger than Δ TA values in December. In addition, the influence of perennial urbanization and long water residence time (~60 days, Liu et al., 2004) allowed the northeastern area of the bay to accumulate large amounts of terrestrial materials (high DIC and TA input, organic matter, and others). Under the strong vertical mixing in winter, the upwelling of bottom water would increase the DIC and TA in surface seawater, and the organic matter carried from bottom would further promote aerobic respiration and increase DIC.

After identifying that the main non-temperature processes which caused DIC and TA addition in December were treated sewage input and aerobic respiration, the DIC/TA value was introduced to explain their impacts on $p\text{CO}_2$. The DIC/TA value can directly indicate the relative abundance of carbonate species (e.g., HCO_3^- and CO_3^{2-}) in seawater. As such, for a specific temperature and pressure, seawater surface $p\text{CO}_2$ is correlated with this ratio (Wang et al., 2013). The DIC/TA value of treated sewage (1.03) was higher than that of the seawater (0.92~0.97) in the JZB. Therefore, direct treated sewage input could increase the DIC/TA and $p\text{CO}_2$ of seawater in the northeastern

area. Meanwhile, aerobic respiration increased DIC by producing CO_2 directly and had a stronger increase effect on DIC/TA and $p\text{CO}_2$. The significant negative correlation between the npCO_2 (the temperature effect was removed) and DO% ($p < 0.05$) (Figure 11a) indicated that aerobic respiration had a dramatic effect on $p\text{CO}_2$ in the entire bay and it caused the bay to act as a CO_2 source in December. In the northeastern area with the lowest salinity, the degree of DO unsaturation was largest and the effects of treated sewage input were superimposed, so the $p\text{CO}_2$ was highest. As the sea area extended to the mouth area, the degree of DO unsaturation decreased gradually. The decline of aerobic respiration caused a gradual decrease in $p\text{CO}_2$ (Figure 11b). The dominant of aerobic respiration in December may be related to that the strengthened vertical mixing brought organic matters and the moderate temperature favoured the degradation activity of heterotrophic bacteria. The similar phenomenon was reported in the continental shelf off Georgia (USA) and the northern Yellow Sea (Jiang et al., 2010; Xu et al., 2016).

4.4 Primary production promoted the strength of CO_2 sink in winter

The distributions of $\Delta\text{TA}/\Delta\text{DIC}$ in the four cruises from early January to late February are shown in Figure 10c-f. In the northeastern area in early January, $\Delta\text{TA}/\Delta\text{DIC}$ values were similar to those in December, between the ratio lines of aerobic respiration and treated sewage input. This suggested that the DIC additions in this area were still mainly caused by these two processes. However, in the western area in early January and the entire bay in mid-January, all $\Delta\text{TA}/\Delta\text{DIC}$ values were larger than 0.97 (the ratio of the treated sewage-altered ΔTA and ΔDIC), moving toward the ratio line of primary production. Considering the oversaturated DO in these periods and regions, the data indicated that primary production obviously consumed DIC, while the treated sewage input directly added DIC and TA. It is worth noting that the $\Delta\text{TA}/\Delta\text{DIC}$ in these periods and regions were also close to the ratio lines of CaCO_3 dissolution and CO_2 evasion. This resulted from the coupled effects of direct treated sewage input and primary production because the possibility of CaCO_3 dissolution and CO_2 evasion were very low based on the high $\Omega_{\text{arag}}@s_{\text{itu}}$ (>1.80) and appearance of a CO_2 sink (Figures 4, 12). In late January and late February, the degree of DO oversaturation was higher and the $\Delta\text{TA}/\Delta\text{DIC}$ values were closer to the ratio line of primary production, indicating the stronger consumption of DIC from primary production.

Obviously, the non-temperature processes affecting $p\text{CO}_2$ changed from aerobic respiration in December to primary production during January and February, which caused an obvious decrease in $p\text{CO}_2$ in the JZB (Figure 4). In the northeastern area of the JZB in early January, DO remained unsaturated and aerobic respiration dominated and the region still acted as a CO_2 source. However, in the western area in early January and the entire bay during mid-January, late January and late February, DO was oversaturated and primary production dominated. The good correlations of npCO_2 vs. DO% and Chl *a* vs. DO% (Figure 13) indicated that absorption of CO_2 by primary production played an important role in the performance of the CO_2 sink in these periods and regions. In the western area in early January, the DO was slightly oversaturated, and the primary production began to dominate and turned the sea area from a CO_2 source in December into a sink. From mid-January to late January, both DO supersaturation and Chl *a* concentration increased (Figure 5h), and the correlation coefficients (r^2) of npCO_2 vs. DO% and DO% vs. Chl *a* also increased. The enhancement of primary production continuously strengthened the CO_2 sink in the period (Figure 4h). In terms of the direct input of treated sewage, the increase in $p\text{CO}_2$ caused by this process was persistent. However, the DO% was always the highest and the $p\text{CO}_2$ was always the lowest in the northeastern area from mid-January to late February (Figures 4, 5), indicating that strong CO_2 consumption from primary production covered the increase in $p\text{CO}_2$ caused by direct input of treated sewage.

The dominant of primary production in this period may be related to the relatively low seawater temperature. The average seawater temperature had decreased obviously and was below 4 °C since early January and even below 2 °C in late January, which suppressed the activities of aerobic respiration. Meanwhile, under stable hydrologic conditions and nutrient accumulation in winter, the cold algae community, which had strong photosynthetic activity and was acclimatized to low temperatures, often exhibited a vigorous growth in the JZB in January and February (Li and Sun, 2014; Sun et al., 2011a; Wu et al., 2004). This is also the reasons for the vigorous growth of phytoplankton in the nearshore areas of Hokkaido (Japan) and Blanca (Argentina) (Popovich et al., 2008; Sakamoto et al., 2008). The weakening of feeding pressure caused by low temperatures may be another reason. In Narragansett Bay, Oviatt et al. (2002) noted that the feeding effect from

zooplankton and filter feeders was inhibited and algal blooms usually occurred when the seawater temperature was below 3 °C. In Massachusetts Bay, Keller et al. (2011) found a good negative correlation between average Chl *a* concentration and seawater temperature during winters from 1995 to 1999 and they emphasized the control of zooplankton feeding on algal blooms.

4.5 The coupled effects of primary production and CaCO₃ precipitation on the *p*CO₂ in March

In March, all $\Delta\text{TA}/\Delta\text{DIC}$ values fell in the third quadrant, basically between the ratio lines of primary production and CaCO₃ precipitation (Figure 10g). Combined with oversaturated DO and high $\Omega_{\text{arag@situ}}$ (2.28~2.53, Figure 12g), it could be inferred that the removal of DIC and TA was mainly caused by primary production and CaCO₃ precipitation. Compared to late February, both the DO oversaturation and the Chl *a* concentration decreased obviously in this period (Figure 5h). Thus, the weakening of primary production was an important factor causing the increase in *p*CO₂ in March. Meanwhile, *np*CO₂ showed no correlation with DO% (Figure 14a), indicating the reduced influence of primary production on the spatial distribution of *p*CO₂. In terms of CaCO₃ precipitation, this process consumed twice TA of DIC, and it further increased the *p*CO₂ levels in March. Considering that primary production consumed DIC but hardly affected TA, the degree of TA removal (ΔTA) could indicate the strength of CaCO₃ precipitation in the period. As shown in Figure 14b, *np*CO₂ was the highest in the northern area, where the TA removal was the largest (~25 $\mu\text{mol/kg}$). As the sea area extended to the mouth area, TA removal and *p*CO₂ showed a decreasing trend. Obviously, the release of CO₂ from CaCO₃ precipitation had a certain influence on the spatial distribution of *p*CO₂ in March. Despite this, the losses of DIC and TA in March were all < 30 $\mu\text{mol/kg}$, indicating the small intensity of primary production and CaCO₃ precipitation. Moreover, due to the opposite effects on *p*CO₂ from the above two processes, the *np*CO₂ differences between the stations in this period were small, less than 30 μatm . In summary, in March, primary production and CaCO₃ precipitation together affected the concentration and spatial distribution of *p*CO₂ in the JZB.

The primary production may be constrained by the insufficient supply of nutrients in the bay in March. According to the observation between 2004 and 2008 (Sun et al., 2011b), the nutrient concentration in the JZB showed a gradual decrease from December to March and reached the minimum of < 0.2 mg/L in March. Meanwhile, the increase of feeding pressure caused by higher

seawater temperature also reduced the phytoplankton biomass (Zhang et al., 2005). The appearance of CaCO_3 precipitation in March may be related to the previously strong primary production in January and February. This is because large amounts of CO_2 consumption from primary production can increase the concentration of CO_3^{2-} and promote the rise of Ω_{arag} , which could increase the possibility of CaCO_3 precipitation (Kim et al., 2013; Xue et al., 2017). Meanwhile, the seawater temperature rose, and clams began to grow in spring (Zhang et al., 2005). The northern area of the JZB, where TA removal is the greatest, is an important breeding area for shellfish (*Ruditapes philippinarum*) in Qingdao, indicating that the appearance of CaCO_3 precipitation may be associated with human shellfish farming activities.

In summary, from aerobic respiration in December to primary production during January and February, and then to the weaken of primary production and the presence of CaCO_3 precipitation in March, the transition of non-temperature processes changed the JZB from a CO_2 source to sink and then to a weak sink throughout the winter. At the same time, the water temperature gradually decreased from December to late January and then increased until March, which suggested that the direction of temperature effect on $p\text{CO}_2$ was consistent with the non-temperature effect in most periods and temperature variation further expanded the $p\text{CO}_2$ variation range. Finally, according to the climatological mean wind speed in Qingdao from December to March (5.6 m/s, Yuan et al., 1996) and the average atmospheric CO_2 concentration (408 μatm) in the Tae-ahn Peninsula station from December 2015 to March 2016, the gas transfer velocity formula of Sweeney et al. (2007) was used to calculate the sea-air exchange fluxes of CO_2 (FCO_2). Overall, the JZB appeared as a sink of atmospheric CO_2 throughout the winter, with the average FCO_2 of $-3.8 \text{ mmol m}^{-2} \text{ d}^{-1}$. In December, the average FCO_2 of the two cruises was $3.0 \text{ mmol m}^{-2} \text{ d}^{-1}$. Then the bay turned into an atmospheric CO_2 sink and the strength of sink continued to increase, from $-6.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ in early January to $-15.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ in late February. In March, the sink strength decreased obviously and the FCO_2 came to $-1.1 \text{ mmol m}^{-2} \text{ d}^{-1}$.

5. Conclusions

In the JZB from December to March, the mutual effect of non-temperature processes among aerobic respiration, primary production and CaCO_3 precipitation were the main intrinsic driving

forces for the $p\text{CO}_2$ variation. Meanwhile, the direction of temperature effect on $p\text{CO}_2$ was consistent with the non-temperature effect in most periods. In December, the higher seawater temperature and the dominance of respiration resulted in the bay acting as a CO_2 source. From early January to late January, with the decrease in $p\text{CO}_2$ caused by cooling, primary production of cold algae increased obviously and the Chl *a* concentration peaked in late February, with the consequence that the JZB became a larger CO_2 sink. In March, the seawater temperature rose, and the strength of CO_2 sink weakened obviously. In this period, with the decrease of primary production, the release of CO_2 from CaCO_3 precipitation appeared. The offsetting of these two processes resulted in a minor difference of the distribution of $p\text{CO}_2$. The strong biogeochemical process occurred widely in the mid-latitude coasts in winter, and its marked impact on seawater $p\text{CO}_2$ should not be ignored. To further improve our understanding of CO_2 sink/source change process and the influence factors in coastal waters, more field studies are still largely needed.

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Figure captions

Figure 1. Study area and survey stations. Solid black circles represent the sampling stations and white stars represent wastewater treatment plants. The gray scale shows water depth.

Figure 2. Variations in seawater surface salinity and temperature during the seven cruises in the JZB. The solid black and open blue squares represent the average seawater surface temperature and salinity. The upper and lower error bars represent the maximum and minimum of seawater surface temperature (salinity) in the cruise. The thick gray line represents the daily average seawater temperature in the JZB from December to April during the period of 2008-2016. The daily seawater temperature data were from FRA-JCOPE2 reanalysis data in Japan (<http://www.jamstec.go.jp/jcope/htdocs/e/home.html>) and were calculated using the JCOPE2 model according to satellite data (for more method details, please refer to Miyazawa et al. (2017)).

Figure 3. Spatial distributions of seawater surface salinity and temperature during the seven cruises in the JZB. The isoline represents salinity and the color scale shows temperature.

Figure 4. Spatial distributions of seawater surface $p\text{CO}_2$ during the seven cruises in the JZB (a-g). Mean $p\text{CO}_2$ during the seven cruises and the upper and lower error bars represent the maximum and minimum of $p\text{CO}_2$ in each cruise (h).

Figure 5. Spatial distributions of seawater surface DO% and Chl a during the seven cruises in the JZB (a-g). The isoline represents Chl a and the color scale shows DO%. The mean DO% and Chl a during the seven cruises and the upper and lower error bars represent the maximum and minimum of DO% (Chl a) in each cruise (h).

Figure 6. Spatial distributions of seawater surface DIC and TA during the seven cruises in the JZB. The isoline represents DIC and the color scale shows TA.

Figure 7. Spatial distributions of $\Delta p\text{CO}_2$ during the seven cruises in the JZB. $\Delta p\text{CO}_2$ represents the difference between $np\text{CO}_2$ and *in situ* $p\text{CO}_2$. The $np\text{CO}_2$ represents the *in situ* $p\text{CO}_2$ normalized to the average seawater temperature for each cruise.

Figure 8. Variations in $p\text{CO}_2$ (solid circle) and $Np\text{CO}_2$ (open circle) during the seven cruises. $Np\text{CO}_2$ represents the average $p\text{CO}_2$ for each cruise normalized to the average seawater temperature of all seven cruises.

Figure 9. Scatterplot of ΔDIC (red triangle) and ΔTA (black circle) with salinity in the JZB during the seven cruises. ΔTA and ΔDIC are deviations calculated using Equations. 8 and 9.

Figure 10. Scatterplot of ΔTA vs. ΔDIC in the JZB during the seven cruises. The four lines represent the theoretical ratio lines altered the ΔTA and ΔDIC by the direct treated sewage input, CaCO_3 precipitation/dissolution, biological process (primary production or respiration) and CO_2 evasion/invasion, respectively. The stations in northeastern area and western area were located in the solid and dotted line circles in c, respectively. Color scale shows DO%.

Figure 11. Scatterplot of $np\text{CO}_2$ vs. DO% (a) and DO% vs. salinity (b) on 13 December (solid circles, y_1) and 21 December (open squares, y_2).

Figure 12. Spatial distributions of seawater surface $\Omega_{\text{arag@situ}}$ during the seven cruises in the JZB.

Figure 13. Scatterplot of $np\text{CO}_2$ vs. DO% (a) and DO% vs. Chl *a* (b) in western area in early January (solid triangles, y_1) and the entire bay in mid-January (open circles, y_2), late January (solid squares, y_3) and late February (stars, y_4).

Figure 14. Scatterplot of $np\text{CO}_2$ vs. DO% (a) and $np\text{CO}_2$ vs. ΔTA (b). The open circles represent the stations in northern area of the JZB.

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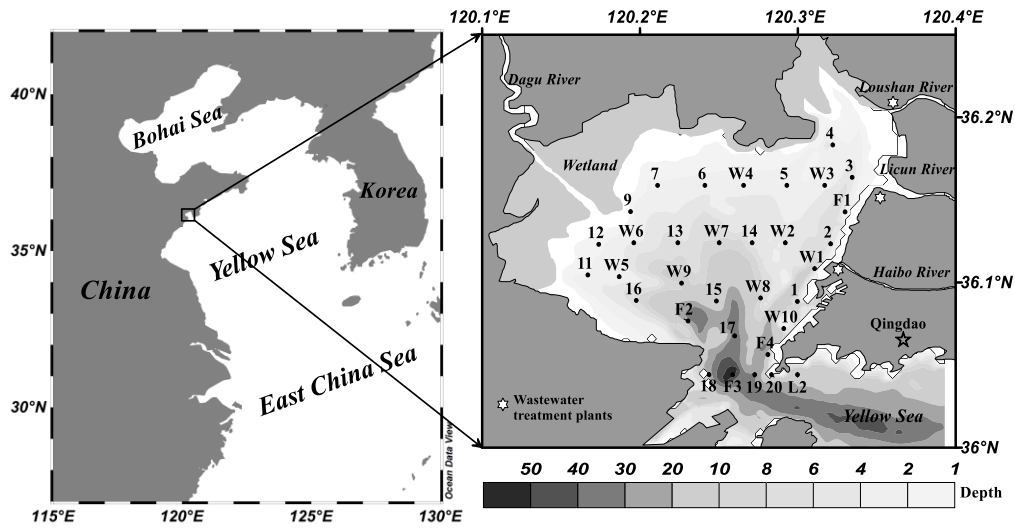
767 **Table. 1.** Summary of the sampling cruises. In late February, we only referenced the data covering
768 our research stations.

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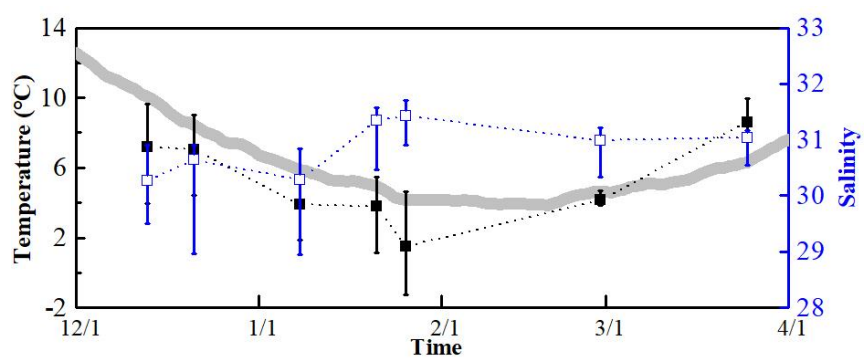
770 **Table. 2.** The values of salinity, DIC and TA of ocean end-member in each cruise during winter in
771 the JZB.

Figures

Figure 1.



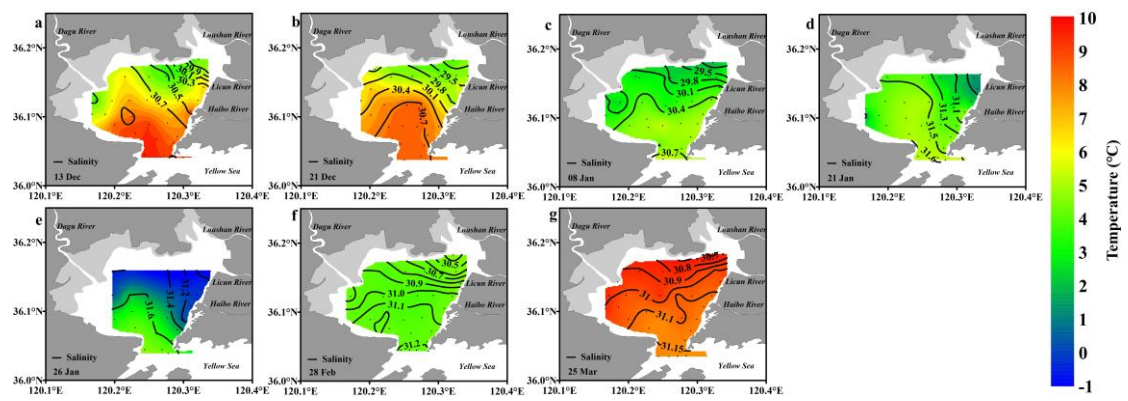
775 **Figure 2.**



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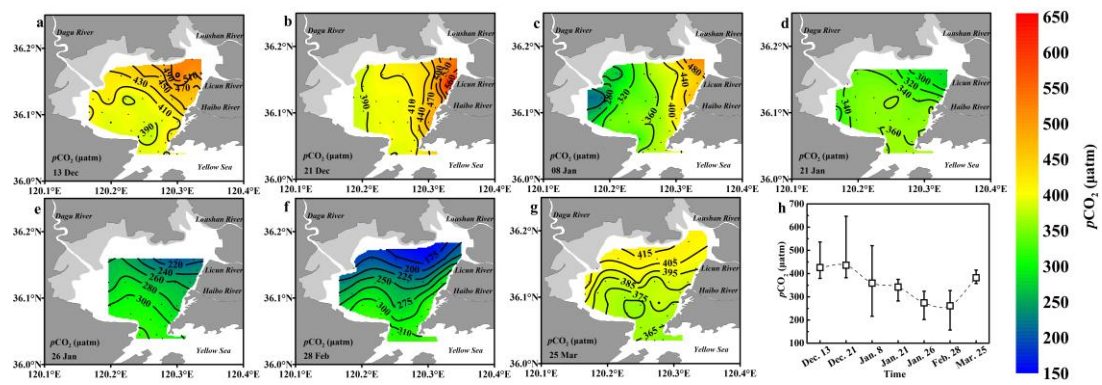
778 **Figure 3.**



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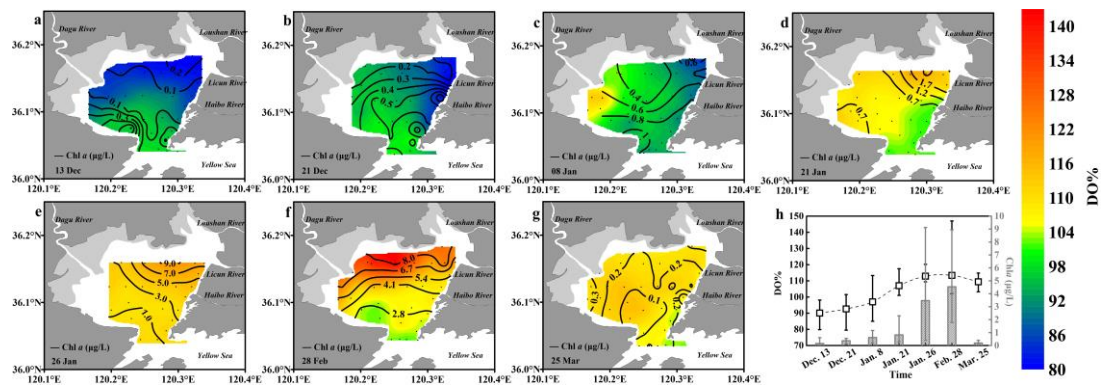
781 **Figure 4.**



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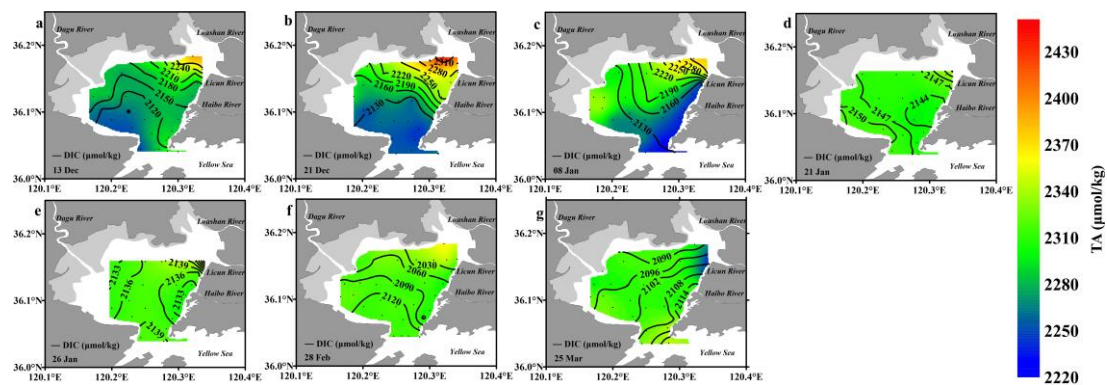
784 **Figure 5.**



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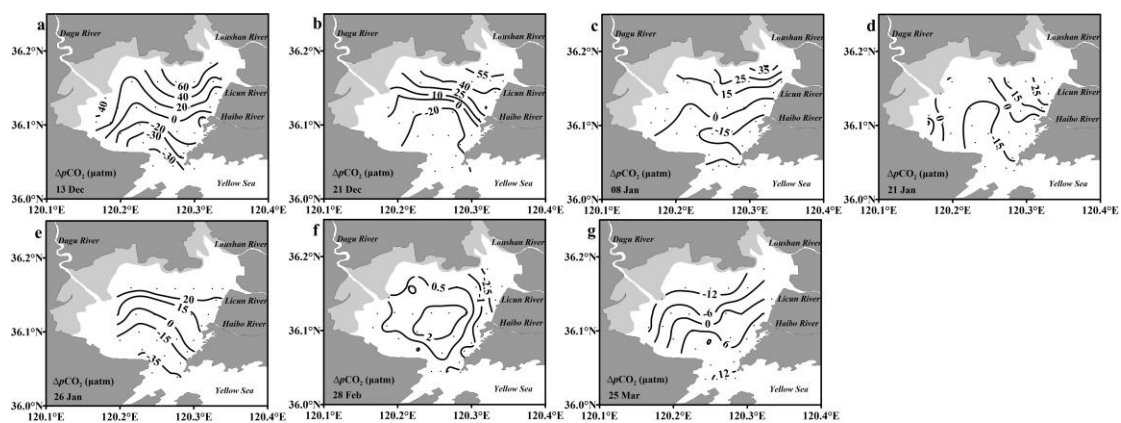
787 **Figure 6.**



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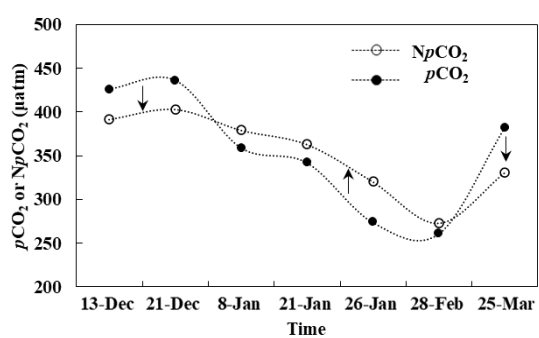
790 **Figure 7.**



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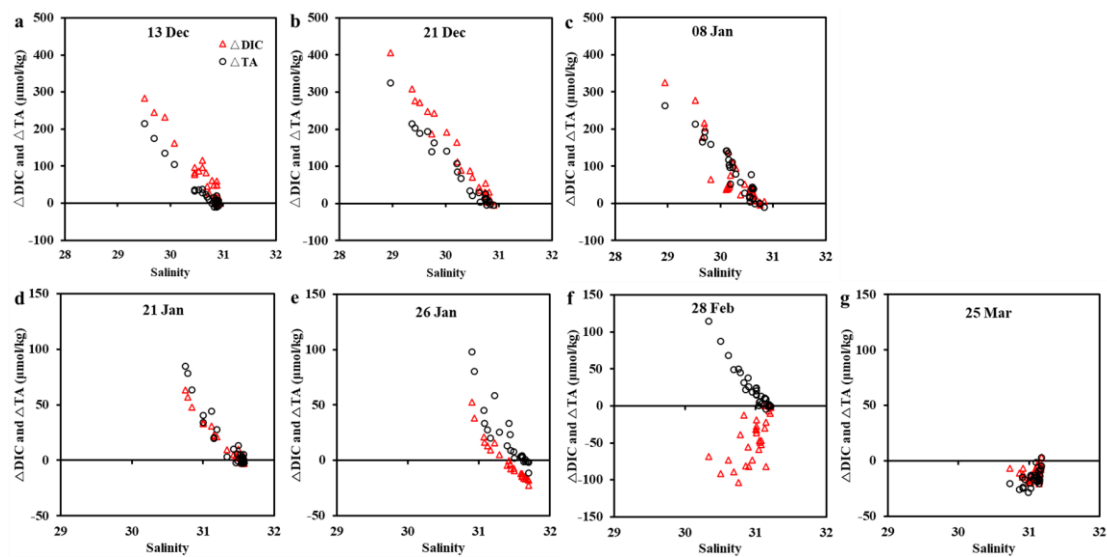
793 **Figure 8.**



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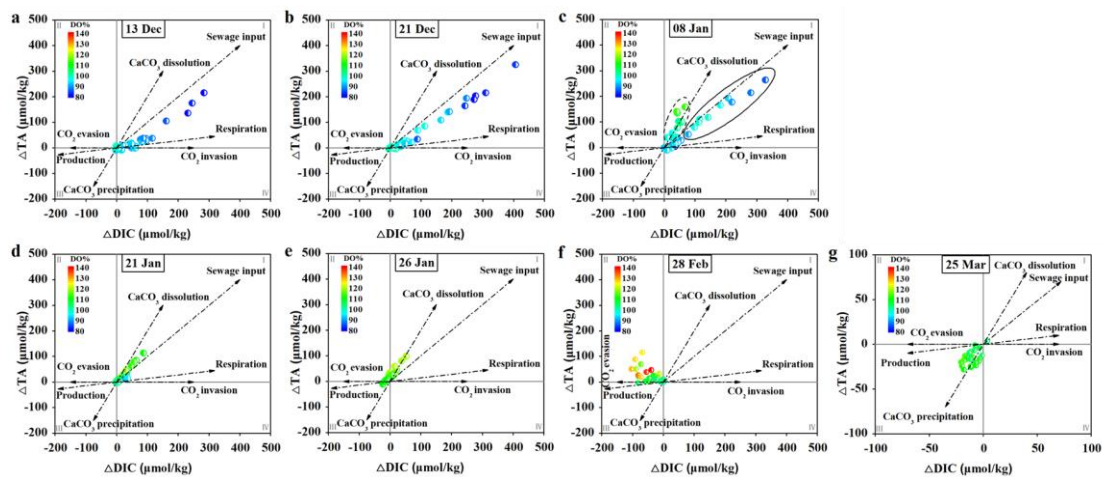
796 **Figure 9.**



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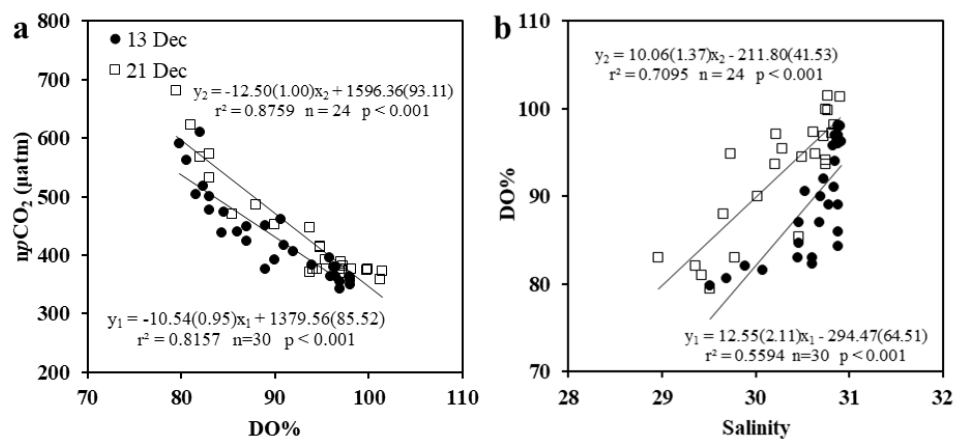
799 **Figure 10.**



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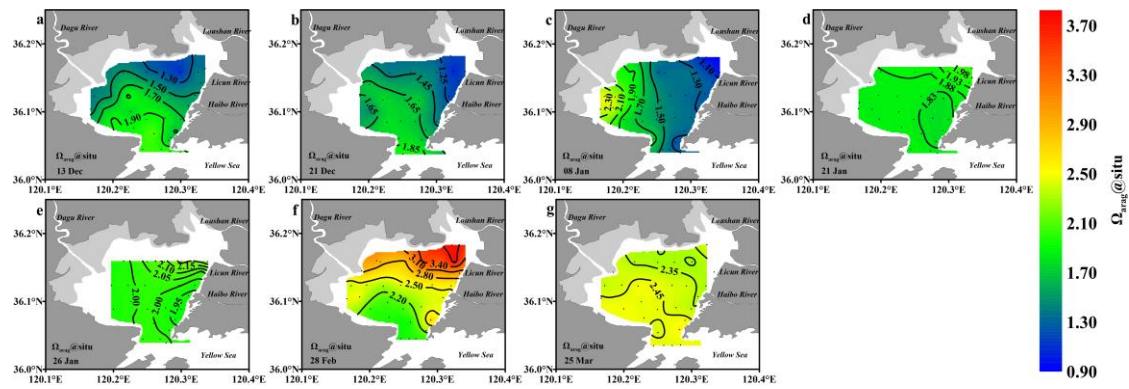
802 **Figure 11.**



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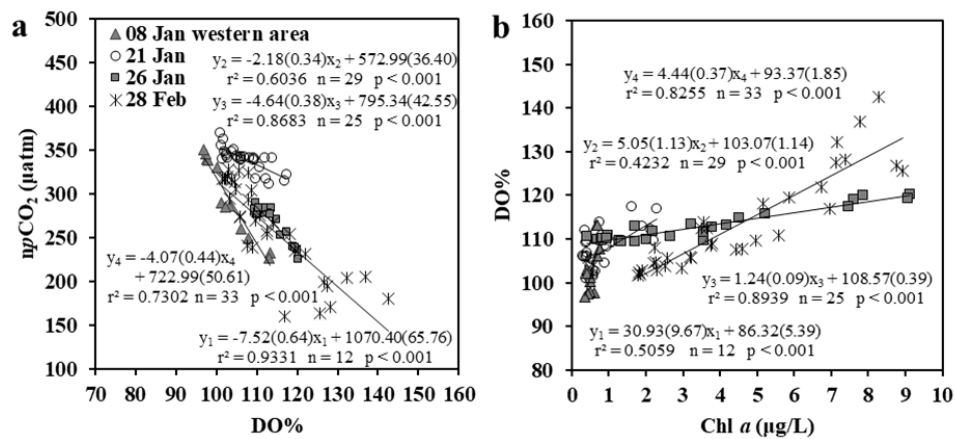
805 **Figure 12.**



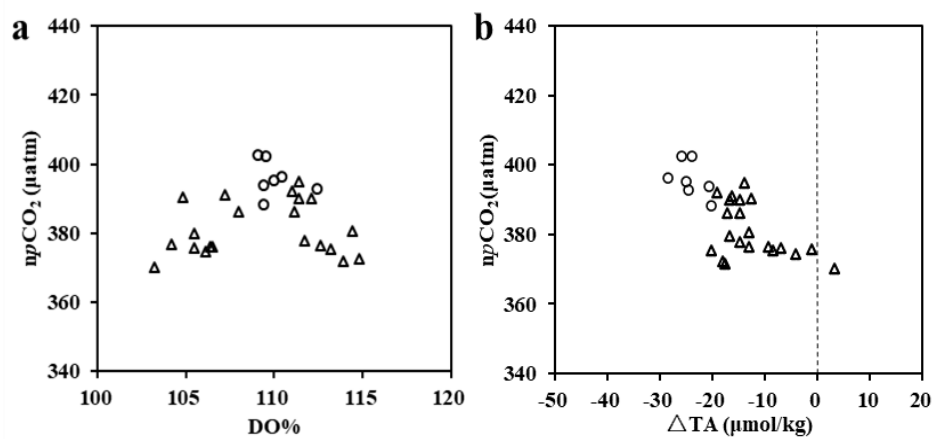
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Figure 13.



811 **Figure 14.**



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814 **Table. 1.**

Cruise	Surveying time	Number of stations	Reference/data source
December	13 Dec. 2014	30	This study
	21 Dec. 2011	24	This study
Early January	08 Jan. 2012	33	This study
Mid-January	21 Jan. 2016	29	Zang et al. (2018)
Late January	26 Jan. 2016	25	Zang et al. (2018)
Late February	28 Feb. 2008	33	Zhang et al. (2012)
March	25 Mar. 2014	30	This study

815

816 **Table. 2.**

Cruise	S _{ocean}	DIC _{ocean}	TA _{ocean}
13 Dec	30.88±0.00	2102±2	2277±1
21 Dec	30.84±0.07	2088±1	2255±1
08 Jan	30.75±0.00	2117±4	2240±0
21, 26 Jan	31.55±0.00	2147±1	2310±0
28 Feb	31.21±0.00	2140±2	2314±1
25 Mar	31.17±0.00	2122±0	2344±0

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